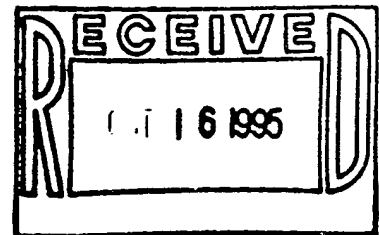


Makes a body - but not for fibers  
+ not for with cyclo -

Japanese Kokai Patent Application No. Hei 1[1989]-138145

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Translated from Japanese by the Ralph McElroy Company, Custom Division,  
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## METHOD FOR MANUFACTURING A SYNTHETIC QUARTZ GLASS ELEMENT

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[Attached amendments have been incorporated into text of  
translation.]

### Claims

1. A method for manufacturing a synthetic quartz glass element characterized by the fact that fine synthetic silica particles are manufactured from a silane compound by a direct flame method, deposited at a thickness of 1-300  $\mu\text{m}$  on a carrier which rotates them during its one cycle, and molten-vitrified.

2. The method for manufacturing a synthetic quartz glass element of Claim 1, wherein the number of rotations of the carrier is set to 3-100 rpm.

3. The method for manufacturing a synthetic quartz glass element of Claim 1, wherein the silane compound is represented by any of (1) a formula  $R_nSiX_{4-n}$  (in which R is a hydrogen atom or an aliphatic monovalent hydrocarbon group, the X are a halogen atom and/or alkoxy groups, and n is an integer of 0-3); (2) a formula  $R^1_nSi(OR^2)_{4-n}$  (in which  $R^1$  and  $R^2$  are the same or different aliphatic monovalent hydrocarbon groups and n is an integer of 0-3); or (3) a formula  $Si_xR_yO_z$  (in which R is the same as before, x is a positive integer of 2 or higher, and y and z are positive integers which are not higher than  $2x + 2$  and  $2x$ , respectively, and are not 0).

#### Detailed explanation of the invention

#### Industrial application field

This invention pertains to a method for manufacturing a synthetic quartz glass element, and in particular, pertains to a method for manufacturing an optical synthetic quartz glass element which is useful for a photolithography apparatus to be used in manufacturing a super-LSI device, since the transmittance of ultraviolet rays is high and there are no three-directional cord or disturbances of transmitted light.

## Prior art

In the manufacture of a semiconductor device, an electronic circuit is projected and exposed on a silicon wafer using a photolithography apparatus; however, along with recent high integration of semiconductor devices, optical sources for photolithography have gradually exhibited short wavelengths. Thus, the use of light in an ultraviolet region with wavelengths of 249 nm and 193 nm is reviewed.

A general optical glass such as conventional BK-7 has been used as a lens material in photolithography apparatuses. However, if the above-mentioned optical source of a short wavelength is used, a general optical glass such as BK-7 cannot be used in terms of the transmittance of light. A quartz glass, in particular, a synthetic quartz glass with favorable transmittance, is used in the ultraviolet region.

However, when there is an optically nonuniform section, called a cord, where the refractive index is locally different in the synthetic quartz glass, if it is used as lens material for a photolithography apparatus, since the cord causes subtle differences in the refractive index, a transfer pattern due to projection and exposure transmitted to the lens is faded, so that a distinct pattern cannot be obtained. Thus, the production of a synthetic quartz glass without a stria is needed.

## Configuration of the invention

This invention pertains to a method for manufacturing a synthetic quartz glass element free from three-directional cord,

not giving rise to the above-mentioned disadvantages, and is characterized by the fact that fine synthetic silica particles are manufactured from a silane compound by a direct flame method, deposited at a thickness of 1-300  $\mu\text{m}$  on a carrier which rotates them during its one cycle, and molten-vitrified.

In other words, these inventors repeatedly reviewed the method for manufacturing a synthetic quartz glass element free from three-directional cord suitable for a lens material for a photolithography apparatus. As a result, it was discovered that when a synthetic quartz was manufactured by forming fine synthetic silica particles by a thermal decomposition or hydrolysis of a silica compound, depositing them on a carrier for rotating them, and molten-vitrifying them, if the deposition rate distribution of the fine silica particles varied, a temperature distribution was generated (Figure 1), so that this changed the structure of the glass. However, in order to avoid this phenomenon, the deposition rate distribution was made more uniform by reducing the amount of raw material gases to be provided to the reaction, so that a synthetic quartz without a substantial stria could not be obtained. In the above-mentioned case where the raw material gas was reduced, since the growth rate of silica was delayed and the productivity was broadly lowered, which was not industrially preferable, a method for making the deposition rate distribution uniform without reducing the amount of raw material gases to be provided was investigated. In other words, it was confirmed that the thickness of silica deposited was 1-300  $\mu\text{m}$ , preferably 1-200  $\mu\text{m}$  during one cycle of the carrier by increasing the number of rotations of the carrier,

Si<sub>3</sub>

6 or fewer O's

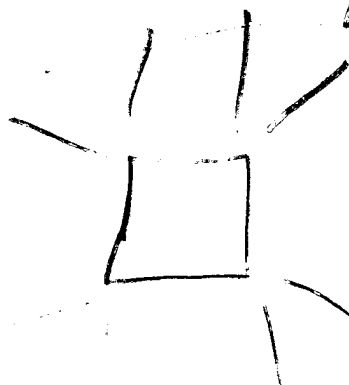
if straight chain  $y = 2x + 2$   
but clearly less than  $2x + 2$  is envisaged

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and the method for adjusting the deposition thickness of silica was advanced, so that this invention was completed.

Next, based on the attached figures, this invention is explained in detail. Figure 1 shows a reference diagram for this invention. Figure 2 shows a vertical cross section of a silica synthesizing method due to a direct flame method in the method of this invention. A mixed gas of oxygen and a silane compound such as tetrachlorosilane, trimethylchlorosilane, trimethylmethoxysilane, or dimethylhydrodienechlorosilane represented by a general formula  $R_nSiX_{4-n}$  (in which, R is a hydrogen atom or an aliphatic monovalent hydrocarbon group to be selected from alkyl groups such as methyl, ethyl, propyl, or butyl, cycloalkyl groups such as cyclohexyl, alkenyl groups such as vinyl and allyl, etc.; the X are a halogen atom and/or alkoxy groups such as methoxy and ethoxy; and n is 0-3); an alkoxy silane such as methyltrimethoxysilane, tetramethoxysilane, or tetramethoxysilane represented by a general formula  $R^1_nSi(OR^2)_{4-n}$  (in which R<sup>1</sup> and R<sup>2</sup> are the same or different aliphatic monovalent hydrocarbon groups to be selected from alkyl, cycloalkyl, alkenyl, etc.; and n is 0-3); or a siloxane such as hexamethyldisiloxane represented by a general formula  $Si_xR_yO_z$  (in which R is the same as before; x is a positive integer of 2 or higher; y and z are positive integers which are not higher than  $2x + 2$  and  $2x$ , respectively, and are not 0) is supplied to oxygen and hydrogen gas from gas inlets 5,6 to ignite and make oxyhydrogen flame 1. Then, the flame 1 is blown to a refractory carrier 2 such as carbon and quartz glass, and silica generated by thermal decomposition or hydrolysis of the silane compound is

if it is less than  $2x + 2$   
it means NO end groups  
which means -Cyclo!



Linear chains  
cyclic

deposited on the carrier 2, so that a silica glass rod 3 is manufactured.

However, in this case, in the above-mentioned manufacturing method of Figure 2, if the growth rate of the synthetic quartz glass is set to 30 mm/h and the number of rotations of the carrier 2 is set to 0.7 rpm, the deposition thickness per one rotation becomes 700  $\mu\text{m}$ , and regular, weak cords are detected. If the number of rotations of the carrier 2 is set to 1.5 rpm, the deposition thickness becomes 400  $\mu\text{m}$ , and the cords are weak as shown in Figure 3(A). However, even so, the cords are not eliminated yet. On the other hand, if the number of rotations of the carrier is set to 3 rpm, the deposition thickness of silica becomes 200  $\mu\text{m}$ , and in this case, as shown in Figure 3(B), the cords are not seen. It is found out that three-directional cords are eliminated.

Therefore, in the method of this invention, in synthesizing a silica glass by a well-known direct flame method, the growth of the silica glass is carried out under the condition in which the growth thickness in the carrier or a silica rod deposited on the carrier is 1-300  $\mu\text{m}$ , preferably 1-200  $\mu\text{m}$  during one rotation of the carrier. Furthermore, at the moment, the number of rotations of the carrier is set to 3-100 rpm, in particular, 3-20 rpm. As the condition for setting the growth thickness of silica to 300  $\mu\text{m}$  or less, the number of rotations of the carrier may be determined considering the diameter of a silica glass to be manufactured by the growth of silica, the growth rate of silica to be deposited, the amount of silane compound supplied, etc. Thus, the synthetic silica glass to be obtained is free of three-directional cords, and therefore, a lens material suitable



for a photolithography apparatus using ultraviolet light with a short wavelength can be easily and efficiently obtained, which is industrially advantageous.

Next, the application examples of this invention are mentioned. Parts in the examples refers to parts by weight [sic].

#### Application Example 1 and Comparative Example 1

5 kg/h silicon tetrachloride gas, 15 Nm<sup>3</sup>/h [sic] oxygen gas, and 30 Nm<sup>3</sup>/h hydrogen gas were supplied to an oxyhydrogen flame generator and ignited, so that a silica was synthesized. It was blown to a carrier made of quartz glass, and while the carrier was rotated at 3 rpm, 36 mm/h (200 μm per one rotation) silica was deposited and molten-vitrified, so that a quartz glass was manufactured. The quartz was free of three-directional cord.

However, for comparison, when the silica was deposited and vitrified under the same condition as above except for setting the number of rotations of the carrier to 1.5 rpm, since the growth thickness of the fine silica particles was 400 μm per one rotation, cords were regularly detected at a minute interval of 1.0 mm or less in the silica rod.

Also, a lens material was cut out of the quartz glass obtained, and a lens was manufactured from it for trial. As a result, in a lens free of three-directional cords, distinct images were obtained. However, when the lens material manufactured from the quartz glass obtained in the comparative

example was used, a prescribed focusing range was deviated from, and images were faded, which was disadvantageous.

#### Application Example 2

Using 2 kg/h methyltrimethoxysilane instead of the silicon tetrachloride in Application Example 1, 10 Nm<sup>3</sup>/h oxygen gas, and 20 Nm<sup>3</sup>/h hydrogen gas, fine silica particles were manufactured. When the number of rotations of the carrier was set at 20 rpm and the fine silica particles were deposited at 24 mm/h and molten-vitrified, the growth thickness of the fine silica particles per one rotation was 20 μm. The quartz silica was free of three-directional cord.

#### Application Example 3

The generation of silica due to the oxyhydrogen flame was carried as in Application Example 2. When the number of rotations of the carrier was set at 90 rpm and the fine silica particles were deposited at 16 mm/h and molten-vitrified, the growth thickness of the fine silica particles per one rotation was 3 μm. The quartz silica was free of three-directional cords.

#### Brief explanation of the figures

Figure 1 shows a deposition state of fine silica particles in manufacturing a synthetic quartz by a conventional method. a) is its vertical cross section, and b) is its horizontal cross

section. Figure 2 shows a vertical cross section of a synthetic quartz manufacturing apparatus for carrying out the method of this invention. Figure 3 is a vertical cross section which shows cord in the synthetic quartz rod obtained by this method. (A) shows the comparative example, and (B) shows the synthetic quartz obtained the method of this invention.

- 1 Flame
- 2 Carrier
- 3 Silica glass rod
- 4 Oxyhydrogen flame generator
- 5, 6, 7 Gas inlets

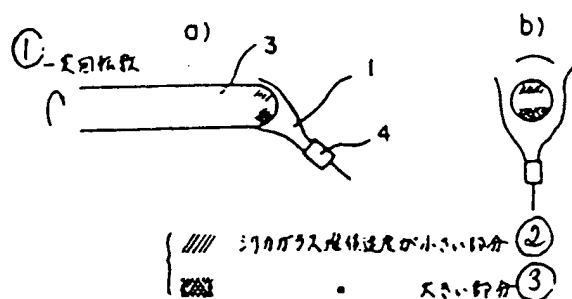


Figure 1

- Key: 1 Constant number of rotations  
 2 Part in which the deposition rate of a silica glass is small  
 3 Part in which the deposition rate of a silica glass is large

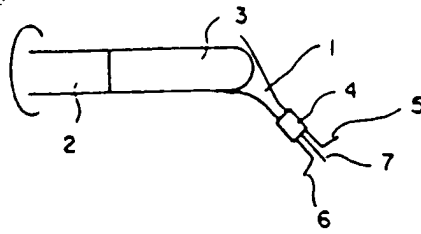


Figure 2

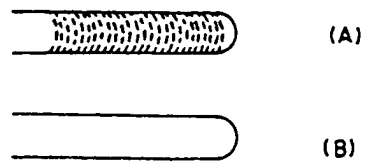


Figure 3